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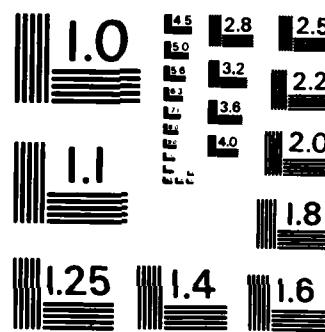
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A STUDY OF THE MECHANISM OF POPULATION OF HIGH LYING ROTATIONAL STATES  
IN HYDROGEN HALIDES

Final Report

Eric Weitz

8/30/85

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4a. Statement of Problem Studied

Hydrogen halides can be made to produce molecular gas lasers which span a wide range of frequencies in the near- to mid-infrared.<sup>1</sup> In particular, the HF laser has been used for a wide variety of applications ranging from scientific to military. Laser action in these systems is typically produced via a chemical reaction of the appropriate halogen atoms with H<sub>2</sub> (D<sub>2</sub>) or via photoelimination of HX (DX) from an appropriate precursor. Though these laser systems are in wide use, a variety of aspects of their operation are not well understood.

For example, in the early 1970s it was found that pure rotational laser action could be produced via photoelimination of hydrogen halides from precursors that also produced vibration-rotation laser action.<sup>2</sup> Despite the discovery of this new class of lasers over ten years ago it is still not clear how these high rotational states, from which pure rotational laser action occurs, are produced. It is also not yet clear what the ramifications the production of these high J states have on the efficiency of HX vibration-rotation lasers.

Another area that impacted on HX lasers involved the observation that vibrational relaxation for many species in cryogenic rare gases was slow.<sup>3</sup> This observation coupled with the broad homogeneously broadened linewidths in these liquids suggested that it might be possible to produce a new class of lasers; liquid lasers. These lasers would potentially be tunable over the broad liquid bandwidths. The hydrogen halides are obvious candidates for this type of a system.

Our objective in the studies supported under contract #DAAG 29-82-K-0125 was to obtain information on energy transfer in hydrogen halides that would

lead to optimization of existing laser systems and point the way toward new laser systems. To effect these goals two parallel lines of investigation were initiated, the results of which are summarized in the next section.

4b. Summary of Results

As indicated in section 4a, two lines of investigation were pursued involving energy transfer in hydrogen halides. The results of energy transfer studies involving hydrogen halides in rare gas liquids will be discussed first.

It has been observed in recent years that relaxation of small molecules in cryogenic liquids is often quite slow; slow enough to allow for the study of relaxation processes via infrared fluorescence techniques.<sup>3</sup> Using these techniques a variety of systems have been studied. Primary objectives in these studies were to determine the relaxation behavior of small molecules and to compare their relaxation behavior in liquids with corresponding relaxation processes in the gas phase.<sup>3</sup> The objective here was to determine if and how well molecules in rare gas liquids follow isolated binary collision (IBC) models which, in the simplest form, state that the liquid phase relaxation rate can be determined from the gas phase relaxation probability at a given temperature by multiplying this probability by the number of collisions in the liquid phase.<sup>4</sup> Our objectives were similar; to determine actual rates for vibrational relaxation processes in liquid and to see how well the rates of these processes could be explained via IBC models. A particularly interesting area of investigation relevant to these points is the measurement of V-V rates in liquids where, due to a change in the microscopic dynamics of the V-V process, simple IBC predictions may fail. Our experiments also focused on hydrogen halides.

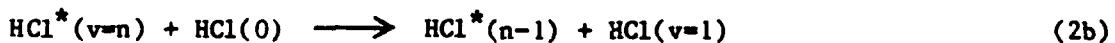
In our experiments we create vibrationally excited hydrogen halides via one of two methods. We either photodissociate HCl with an ArF laser where the initial step



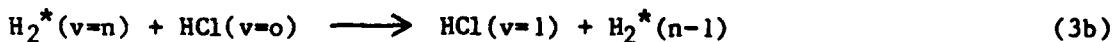
is followed by recombination steps to yield  $\text{HCl}^*$ , vibrationally excited HCl. Alternatively, we produce  $\text{HCl}^*$  directly via photoelimination of HCl from any of a variety of chloroethylenes such as



When  $\text{HCl}^*$  is produced via the first mechanism, a question which we have studied is exactly how  $\text{HCl}^*$  is produced. After a significant amount of study involving time, concentration and power dependent studies of the  $\text{HCl}^*$  rise-time, we conclude that two recombination schemes may lead to  $\text{HCl}^*$ . These are



and



Our conclusions regarding the production of  $\text{HCl}^*$  is that both processes are likely to contribute to the production of  $\text{HCl}^*$  and the dominance of a given process is a function of the specific set of experimental conditions. The detailed rationale for these conclusions is laid out in reference 5.

This method of production of  $\text{HCl}^*$  has allowed us to measure the V + T/R relaxation rate of  $\text{HCl}^*$  in liquid Xe and Kr by rare gas atom collisions and

HCl-HCl collisions.<sup>6,7</sup> We have also applied this method to DCl\* and have measured its V + T/R rate in liquid Xe.<sup>8</sup> The measured relaxation rates are summarized in table 1. These rates have been compared to the predictions of IBC models with the conclusion that at least the HCl-HCl and DCl-DCl V-T/R relaxation rates are adequately described. The rare gas-HCl and DCl V + T/R rates vary by almost an order of magnitude from IBC model predictions. However, the predictions are based on one room temperature measurement of the relaxation of HCl by Xe and Kr.<sup>9</sup> Thus existing data is not sufficient to conclude the IBC model does not work for HCl or DCl - rare gas collisions in these systems.

Another interesting conclusion involves the relative rates of relaxation of HCl vs. DCl. The HCl vs. DCl V + T/R rates in liquid Xe scale as would be expected based on gas phase data. As discussed in detail in reference 8 this implies that rotational degrees of freedom are important for the relaxation process in the liquid rare gas just as they are in the gas phase. This is interesting since the spectrum of HCl or DCl in liquid Xe shows a pressure induced "Q branch" which implies that rotational motion of the hydrogen halides is altered enough by the solvent to make J no longer a good quantum number for rotation.

V-V rates have also been measured in a number of systems. In these experiments HCl\* is produced via photoelimination from an appropriate chloroethylene parent. Transfer from HCl\* to vinyl chloride and 1,1-dichloroethylene have been measured.<sup>12</sup> In addition the process



has been measured.<sup>13</sup> In all of these cases the rate in the liquid is greater than in the gas phase at the same temperature. In the two former cases it is considerably greater. Reasons for these differences and a discussion of how IBC models apply to V-V processes in solution is contained in references 12 and 13. The rates measured for these V-V processes are summarized in table 2.

In addition to measurements in liquid rare gases we have also measured the rate of relaxation of HCl in solid xenon as a function of temperature.<sup>14</sup> This rate was compared to the rate of relaxation of HCl in liquid Xe just above the melting point and to the rate of relaxation of matrix isolated HCl at 40 K. The rates at 40 K were identical within experimental error. However, the rates just above and below the freezing point of Xe were at least superficially different. This difference can be rationalized by the loss of mobility of HCl on freezing. This loss of mobility eliminates HCl-HCl V-V and V + T/R relaxation channels leaving HCl-Xe V + T/R processes as the only channel. This rate can then be compared to the HCl-Xe component in LXe and these rates are found to agree within experimental error. These experiments also serve to provide a significant extension of the temperature dependence of the rate of relaxation of matrix isolated HCl and to unify the temperature dependence of HCl-Xe relaxation processes over all three phases.

In addition to the above experiments, since atoms are generated in the photolysis of HCl, reactions of these atoms with added chemical species can be studied. We have looked at the reaction of H + Cl<sub>2</sub> which is a reaction that produces a gas phase HCl population inversion which leads to laser action.<sup>15</sup> In the liquid phase the reaction also occurs producing HCl\* though we have not as yet looked at the vibrational population distribution. We

have also investigated the reaction of  $H + CO \rightarrow HCO$  and  $H + NO \rightarrow HNO$  in liquid rare gas solution.<sup>16</sup>

The net effect of these studies is that we have significantly increased the data base on relaxation processes in liquid rare gases. We have also increased our predictive capabilities with regard to scaling of gas phase  $V \rightarrow V$  and  $V \rightarrow T/R$  rate constants. This increased data base and improvement of level of understanding of relaxation processes in solution will help greatly in modeling processes involving vibrationally excited molecules in solution -- including solution phase lasers.

The other area of investigation involved looking at highly rotationally excited HF produced via photoelimination of HF from  $C_2H_5F$ .<sup>17</sup> This was done in an effort to determine if high J states in HF were formed in the nascent photodissociation process or produced via relaxation of HF  $v=n \rightarrow n-1$  with the concomitant products of high J states. Experiments were performed via TEA  $CO_2$  laser excitation of  $H_3CCH_2F$  and observation of infrared emission from the climates HF's pure rotational or vibration-rotation transitions. The pure rotational transitions observed were in the  $14-20 \mu$  region which corresponded to  $\Delta J$  transitions in  $v=0$  originating from J states between  $J = 12$  to  $\sim 16$ . Vibration-rotation transitions that were observed were from the R branch of the 1-0 HF transition near  $2.4 \mu$ . The R branch forms a band head in this region and emission observed was from J transitions in the band head which consisted of approximately 10 J states. Unfortunately, in all studies, emission for HF J states was at least partially observed by background emission from other species. In the far IR, though, the ethyl fluoride parent and the ethylene co-photoproducts did not have a band in this region; acetylene does. Acetylene is produced in small quantities by photofragmen-

tation of  $C_2H_4$  which either absorbs additional photons to lose  $H_2$  or is already sufficiently energized by the initial MPIR process to lose  $H_2$ . In any case, the amount of emission in this region from  $C_2H_2$  was determined to be comparable to the amount of emission from HF. Since our filters were not narrow enough to discriminate HF emission from  $C_2H_2$  emission, these signals were by necessity convoluted with each other. This made measurements of relaxation times that could be assigned to a specific process very difficult. However the risetime of the IR emission signal was prompt following the laser pulse. Similarly, emission in the  $2.4 \mu$  region was observed to overlap with a band of ethylene. Emission from this band was sufficient to observe the fall times of the HF high J signals and similarly made it difficult to measure the rate of relaxation of high J states in  $v=1$ . However, again the rise of emission was prompt. Thus, though we could not come to conclusions regarding the relaxation rate of high J states, we could conclude that emission from high J states of HF was prompt and thus that a significant fraction of HF molecules that are produced in high J states are born in those states (at least in  $v=1$  and  $v=0$ ). To be more quantitative would require modeling of the system's kinetics which would also require knowledge of relaxation rates of high J states which were unobtainable in our experiments. Nevertheless, the conclusion reached is an important one for modeling rotational laser systems.

4c) Publications

Vibrational Relaxation of HCl in HCl/Liquid Xenon Mixtures  
J.T. Knudtson and E. Weitz  
Chem. Phys. Letters., 104, 71 (1984).

Relaxation of HCl in Liquid Xenon Solution by Vibration-Vibration Energy Transfer

J. T. Knudtson, Yannis P. Vlahoyannis, Herman Krueger and Eric Weitz  
J. Chem. Phys., 82, 4381 (1985).

Infrared Spectra and Bandstrengths of the Fundamental and First Overtone of HCl and DC1 in Liquid Xenon Solution

J. T. Knudtson and E. Weitz  
J. Chem. Phys., 83, 927 (1985).

Relaxation of vibrationally excited HCl in Solid Xe

H. Krueger, J. T. Knudtson, Y. Vlahoyannis and Eric Weitz  
Chem. Phys. Letters - in press

Vibrational Energy Transfer in HCl Liquid Xenon Solutions

J. T. Knudtson, E. Weitz, Y. P. Vlahoyannis and H. Krueger  
Proceedings of the Society for Optical and Quantum Electronics for Lasers - (1984) - in press

Vibration-Vibration Energy Transfer Processes in Liquid Xenon: A Measurement of the Rate Constant for  $HCl(v=2) + HCl(v=0) \rightarrow 2HCl(v=1)$   
V. P. Vlahoyannis, H. Krueger, J. T. Knudtson and E. Weitz  
Chemical Phys. Letters - in press

The Production and Relaxation of vibrationally excited HCl in Liquid Xenon Solution

H. Krueger, Y. P. Vlahoyannis, J. T. Knudtson and E. Weitz  
To be published

Vibrational Relaxation of DC1( $v=1$ ) in Liquid Xenon at 211°K

H. Krueger, J. T. Knudtson, Y. P. Vlahoyannis, and E. Weitz  
To be published

Vibrational Relaxation of HCl( $v=1$ ) in Liquid Krypton

H. Krueger, J. T. Knudtson, Y. P. Vlahoyannis and E. Weitz  
To be published

Vibrational Energy Transfer Studies of HCl and DC1 in Condensed Rare Gas

Ph.D. Thesis - Herman Krueger 9/85

4d. Participating Scientific Personnel

Eric Weitz - principal investigator

Herman Krueger - graduate student - Ph.D. 8/85

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Yannis P. Vlahoyannis - postdoctoral research associate

Tom Knudtson - visiting professor

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15. H. Krueger, Ph.D. Thesis, Northwestern University, Evanston, Illinois, 9/85.
16. H. Krueger, J. T. Knudtson and E. Weitz, unpublished data.
17. H. Krueger and E. Weitz, unpublished data.

Table I  
Vibrational Relaxation Rates\*

excited species	Xe	Kr	HCl	DCl
	(5.6 2.1) $\times 10^6$	(1.6 .2) $\times 10^6$	(1.75 .09) $\times 10^{10}$ (LKr -190 K)	-
HCl*			(1.8 .3) $\times 10^{10}$ (LXe -205 K)	
DCl*	(1.3 5) $\times 10^6$	-	-	(5.0 1.2) $\times 10^9$

\*Units in table are  $\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$ .

Table II  
Vibration-Vibration Energy Transfer Rates\*

excited species	collision partner	HCl(v=0) in Xe	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> in Xe	C <sub>2</sub> H <sub>3</sub> Cl in Xe
	HCl(v=1)	-	8.1 1.1 x 10 <sup>11</sup>	7.8 1.3 x 10 <sup>11</sup>
	HCl(v=2)	2.8 0.1 x 10 <sup>12</sup>	2.6 .3 x 10 <sup>12</sup>	-

\*Units in table are cm<sup>3</sup> mole<sup>-1</sup> s<sup>-1</sup>.

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